

## Density Functional Theoretical Study on the Substituent Effect in Aryl Halide Oxidative Additions to a Rh Pincer Complex

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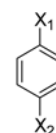
**Key Words** : DFT, Oxidative addition, Aryl halides, Rh pincer ligand

Oxidative addition reactions of aryl halides to transition-metal complexes are fundamental reactions in organometallic chemistry.<sup>1</sup> A previous paper reported the results of density functional theoretical (DFT) studies of the oxidative addition of aryl halides to (PNP)Rh fragment **1** (where PNP is the bis(*o*-diisopropylphosphinophenyl)amide “pincer” ligand), which is generated from (PNP)Rh(SPr<sub>2</sub>).<sup>2</sup> Fragment **1** can react with many chemical species, which provides several kinetic and thermodynamic parameters of the reactions, and is useful for comparative studies.<sup>3,4</sup> DFT calculations<sup>2</sup> were performed to determine the Gibbs energy of the reaction for C–X oxidative addition to fragment **1**, and compare the relative stability of the initial adduct and oxidative addition product. In addition, the Gibbs energy of activation of the reactions was calculated. These thermodynamic and kinetic quantities are the key parameters for determining the preference and reactivity toward chemical species. DFT calculations<sup>5</sup> for the Si–X oxidative addition reactions to compound **1** were also performed to compare the thermodynamic and kinetic parameters with those of C–X oxidative additions. Both the thermodynamic and kinetic results were consistent with the published experimental data and computational results reported previously for similar complexes.<sup>4</sup> The reactivity is more favorable compared to carbon compounds, which is also consistent with previous experimental results.<sup>6</sup>

Recently, kinetic studies on the substituent effect on the rate of oxidative addition reactions to compound **1** were reported.<sup>7</sup> *para*-Substituted aryl halides were adopted as the incoming ligands and their reaction rates were monitored. In this study, DFT calculations for the C–X oxidative addition

to compound **1** were carried out to assess the electronic influence of the substituent in aryl halides and test the applicability of the DFT method to a quantitative evaluation of the thermodynamic quantity. The B3LYP/LACVP\*\* level calculations were chosen because the level of theory was applied successfully to oxidative addition/reductive elimination reactions involving organometallic pincer complexes.<sup>8,9</sup>

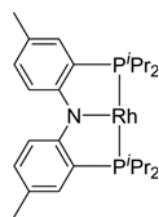
Scheme 2 depicts the aryl halides used in the present work. Table 1 lists the Gibbs energy of activation ( $\Delta G^\ddagger$ ) for the C–X oxidative addition to fragment **1** from B3LYP/6-31G\*\* level calculation. In all aryl halides, the electron withdrawing groups (EWG) accelerate the reaction. As shown in previous work,<sup>2</sup> the transition state (TS) for the reaction is three-centered, where the C–X bond is stretched and M–C and M–X bonds are partly formed, which lies on the continuum of the concerted oxidative addition reaction



X<sub>1</sub> = Cl, Br, and I

X<sub>2</sub> = NH<sub>2</sub>, OMe, Me, F, H, Cl, Br, CF<sub>3</sub>, CO<sub>2</sub>Me, CO<sub>2</sub>Et, and NO<sub>2</sub>

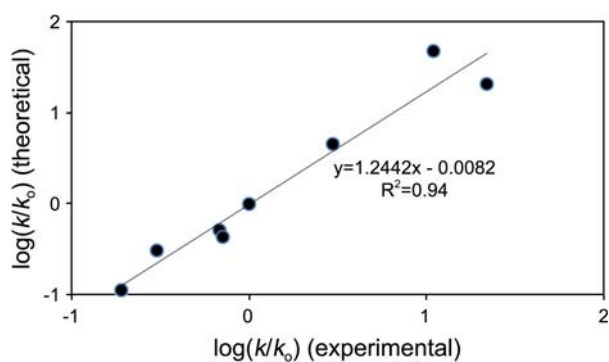
**Scheme 2**



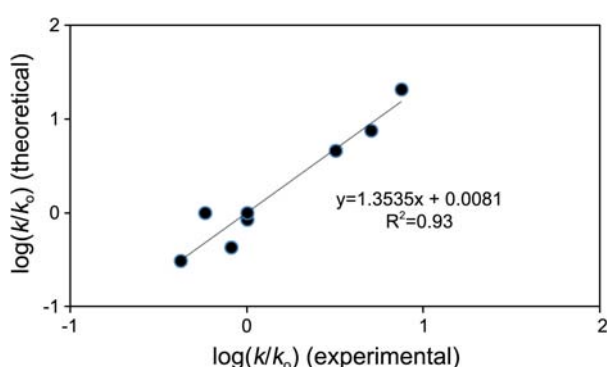
**1**  
**Scheme 1**

**Table 1.** Gibbs energy of activation ( $\Delta G^\ddagger$ ) between compound **1** and aryl halides (unit: kcal mol<sup>-1</sup>)

X <sub>2</sub>	Aryl chloride	Aryl bromide	Aryl iodide
NH <sub>2</sub>	16.2	12.4	13.1
OMe	15.6	11.7	12.9
Me	15.3	12.2	12.9
F	15.4	11.8	12.3
H	14.9	11.7	12.6
Cl	14.0	11.3	12.6
Br	14.0	11.3	11.7
CF <sub>3</sub>	12.6	10.8	11.7
CO <sub>2</sub> Me	13.1	10.5	11.8
CO <sub>2</sub> Et	12.8	10.5	11.5
NO <sub>2</sub>	10.5	9.9	11.4



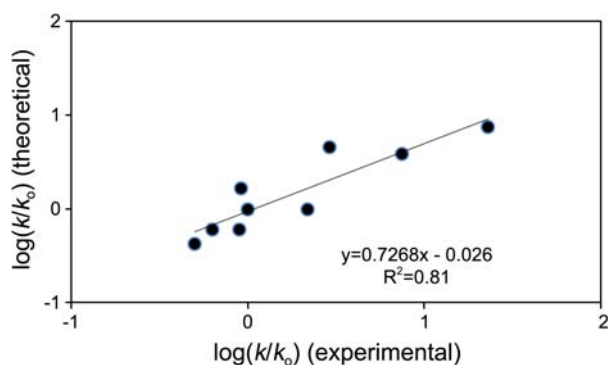
**Figure 1.** Logarithmic values of the relative rate constants for aryl chlorides.



**Figure 2.** Logarithmic values of the relative rate constants for aryl bromides.

toward the nucleophilic aromatic substitution ( $S_NAr$ ) reaction.<sup>7</sup> The EWG withdraws electron density and effectively stabilizes the partial negative charge generated in the aromatic ring in the TS. The Hammett  $\sigma^-$  parameter, which is designated in the case where negative charge buildup in the TS occurs, correlates well with the rate constant.<sup>7</sup>

To make a quantitative comparison with the experiments, the experimental rate was correlated with the computational one. The relative rate constants for the reactions where the rate constants of unsubstituted PhCl, PhBr and PhI were set to unity were compared with the experiments. Arrhenius form is used for the rate constant and the pre-exponential factor is assumed to be the same for all the substituents. The correlation results were good for aryl chlorides and aryl



**Figure 3.** Logarithmic values of the relative rate constants for aryl iodides.

bromides. On the other hand, for iodides, the correlation coefficient was lower than the other cases, partly because the variation in activation energy was only 1.7 kcal mol<sup>-1</sup> for iodides.

In summary, DFT calculations were applied to the oxidative addition reaction of *para*-substituted aryl halides to the pincer type Rh complex. The kinetic results were consistent with the published experimental data. The computational scheme provided a quantitative estimate of the rate constant and qualitative tendency.

### Computational Details

The geometry of each compound was optimized at the B3LYP/LACVP\*\* level of theory using the Jaguar v5.5 suite.<sup>10</sup> The stability of all minima including the intermediates, and transition states (TSs), was evaluated by calculating the standard Gibbs energy of each species at 298.15 K using the following equation.

$$\Delta G = E_0 + \text{ZPE} + \Delta\Delta G_{0 \rightarrow 298\text{K}} \quad (1)$$

The total energy of the molecule at 0 K ( $E_0$ ) was calculated at the optimal geometry from the B3LYP/LACVP\*\* computational level. The zero-point energy (ZPE) and the change in Gibbs energy from 0 K to 298.15 K ( $\Delta\Delta G_{0 \rightarrow 298\text{K}}$ ) were studied at the same level of theory. The thermodynamic quantities were examined according to the rigid-rotor harmonic oscillator approximation using the computed harmonic frequencies from the B3LYP/LACVP\*\* calculations. The local minima and TSs were identified by harmonic frequency analysis from analytical Hessian calculations. The reaction paths were traced from the TSs using the intrinsic reaction coordinate (IRC) method<sup>11,12</sup> to confirm that the reactants and products were correct. The isopropyl groups attached to the phosphorus atoms in all the complexes were replaced with methyl groups to reduce the computational burden.

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